

What is claimed is:

1. A method of forming a film, comprising:

a coating step of forming a film by coating a coating liquid, in which particles or colloids of a starting substance of a film component are dispersed in a solvent, on a surface of a substrate;

5 a first gelling step of, together with carrying the substrate into a sealed chamber, gelling the substrate in a state where the substrate is exposed to a gas containing a solvent vapor of the coating liquid at a first average 10 concentration; and

15 a second gelling step of gelling in a state where the inside of the sealed chamber is filled by a gas containing the solvent vapor of the coating liquid at a second average concentration higher than the first average concentration.

2. The method of forming a film as set forth in claim

1:

wherein a gas to be introduced in the sealed chamber in the first gelling step is controlled such that temperature 20 thereof is close to that inside the sealed chamber.

3. The method of forming a film as set forth in claim 1, further comprising:

preceding the first gelling step,

25 a step of, together with generating a mixed gas of a vapor of a solvent component and a carrier gas, exhausting the mixed gas by switching a valve to exhaust side;

wherein an operation of, in the first gelling step, exposing the substrate to the gas containing the solvent

vapqr of the coating liquid at the first average concentration is carried out by introducing the mixed gas into the sealed chamber by switching the valve.

4. The method of forming a film as set forth in claim
5 1:

wherein the gelling step is a step of heating the substrate.

5. The method of forming a film as set forth in claim
1:

10 wherein the gas is generated by mixing a carrier gas and a vapor of a solvent component;

wherein the first gelling step is carried out by controlling a flow rate of at least one of the carrier gas or the vapor of the solvent component.

15 6. The method of forming a film as set forth in claim
1:

wherein the mixing of the carrier gas and the vapor of the solvent component is carried out at a vaporizer vaporizing a liquid of the solvent component, and the first 20 gelling step is carried out by controlling a flow rate of the liquid of the solvent component being introduced into the vaporizer.

7. The method of forming a film as set forth in claim
1:

25 wherein the first gelling step includes a step of varying continuously a concentration of the vapor of the solvent component.

8. The method of forming a film as set forth in claim

1:

wherein the first gelling step includes a step of mixing intermittently the vapor of the solvent component into the carrier gas.

5 9. The method of forming a film as set forth in claim 1, further comprising:

a step of, up to before exposing the substrate to a gas after carrying the substrate into a sealed chamber, feeding the gas into a sealed chamber in a state where an average 10 concentration of the vapor of the solvent component is higher than an average concentration during the first gelling step.

10 10. The method of forming a film as set forth in claim 1:

15 wherein the first average concentration is a concentration corresponding to a saturated vapor pressure at a substrate temperature during transfer into a chamber; and

wherein the second average concentration is a concentration corresponding to a saturated vapor pressure at a substrate temperature during gelling.

20 11. An aging unit comprises:

a treatment chamber accommodating a substrate formed thereon a film containing a solvent and particles or colloids of a starting substance of a film component;

a heater for heating the substrate;

25 a carrier gas feeding system for feeding the carrier gas toward the treatment chamber;

a solvent dispensing system for dispensing the solvent toward the treatment chamber;

. a mixing system for forming a mixed gas containing a solvent vapor from the carrier gas feeding system and the solvent dispensing system; and

5 a control mechanism for controlling a solvent concentration of the mixed gas.

12. An apparatus of forming a film comprises:

a coating unit for coating, on a surface of a substrate, a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent;

10 an aging unit comprising a treatment chamber for accommodating the substrate formed thereon the film, a heater for heating the substrate, a carrier gas feeding system for feeding the carrier gas toward the treatment chamber, a solvent dispensing system for dispensing the solvent toward the treatment chamber, a mixing system for forming a mixed gas containing a solvent vapor from the carrier gas feeding system and the solvent dispensing system, and a control mechanism for controlling a solvent concentration of the mixed gas; and

20 a solvent replacement unit for replacing the solvent in the film.

13. A method of forming a film, comprising:

a step of forming a film by coating, on a surface of a substrate, a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent;

a step of gelling the particles or the colloids in the film; and

a step of dispensing, on the surface of the substrate,
at least 2 kinds of replacement solvents different from the
solvent by switching them sequentially;

wherein switching of the replacement solvent to be fed
5 is carried out by, after subsequent replacement solvent is
began in dispensing while dispensing a preceding replacement
solvent, stopping dispensing of the preceding replacement
solvent.

14. The method of forming a film as set forth in claim
10 13:

wherein the at least 2 kinds of solvents are dispensed
to the substrate from a common solvent dispensing portion:

15. The method of forming a film as set forth in claim
13:

wherein the at least 2 kinds of solvents are dispensed
15 to the substrate from separate solvent dispensing portions.

16. The method of forming a film as set forth in claim
13:

wherein the step of dispensing by switching
20 sequentially the replacement solvent is a step of dispensing
on the substrate an alcohol, a hydrophobic treatment liquid,
and a solvent of smaller surface tension than solvents
included in the coating liquid in this order.

17. A solvent replacement unit, comprises:

25 a treatment chamber accommodating a substrate formed
thereon a film containing a solvent and particles or colloids
of a starting substance of a film component;

a spin chuck holding the substrate disposed in the

- treatment chamber;
- a plurality of solvent dispensing systems for dispensing solvents to the substrate; and
- a switching device for switching the plurality of
- 5 solvent dispensing systems.
18. An apparatus of forming a film, comprises:
- a coating unit for forming a film by coating a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent on a surface
- 10 of a substrate;
- an aging unit for gelling the film; and
- a solvent replacement unit comprising a treatment chamber accommodating the substrate formed thereon the film containing the solvent and the particles or colloids of the
- 15 starting substance of the film component, a spin chuck holding the substrate disposed in the treatment chamber, a plurality of solvent dispensing systems dispensing the solvents to the substrate, and a switching device switching the plurality of solvent dispensing systems.
- 20 19. A method of forming a film, comprising:
- a step of forming a film on a surface of a substrate by coating a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent under an atmosphere that is filled by a vapor of the
- 25 solvent; and
- a step of gelling the particles or colloids in the film.
20. A method of forming a film, comprising:
- a step of carrying in a substrate from an intake into a

treatment chamber;

a step of closing the intake of the treatment chamber;

a step of filling the treatment chamber by a solvent vapor;

5 a step of coating, on a surface of the substrate, a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in the solvent in the treatment chamber filled by the vapor; and

a step of gelling the particles or colloids in the film.

10 21. The method of forming a film as set forth in claim 20, further comprising:

a step of removing, after the film is spread on the surface of the substrate, while the treatment chamber is being filled by the vapor of the solvent, the film on a circumference portion of the substrate by dispensing a 15 circumference portion of the substrate by dispensing a cleaning liquid for removing the film on the circumference portion of the substrate.

22. A method of forming a film, comprising:

a step of carrying in a substrate into a treatment 20 chamber from an intake and placing it on a rotary stage; a step of closing the substrate intake of the treatment chamber;

a step of filling a vapor of a solvent into the treatment chamber to fill by the vapor;

25 a step of, together with rotating the rotary stage, dispensing, on a surface of the substrate, a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in the solvent to spread the

coating liquid on the surface of the substrate; and
a step of gelling the particles or colloids in the film.

23. The method of forming a film as set forth in claim
22, further comprising:

5 a step of, after spreading the film on the surface of
the substrate, while the inside of the treatment chamber is
being filled by the solvent vapor, dispensing a cleaning
liquid for removing the film on a circumference portion of
the substrate to remove the film on the circumference portion.

10 24. A coating unit, comprises:

• a treatment chamber accommodating a substrate;
a spin chuck holding the substrate disposed in the
treatment chamber;
a coating liquid nozzle for dispensing a coating liquid
15 to the substrate;

• a coating liquid dispensing system for dispensing the
coating liquid in which particles or colloids of a starting
substance of a film component are dispersed in a solvent to
the coating liquid nozzle;

20 a solvent nozzle for dispensing the solvent into the
treatment chamber; and

• a solvent dispensing system for dispensing the solvent
to the solvent nozzle.

25 25. An apparatus of forming a film, comprises:

• a coating unit of forming a film on a substrate
comprising a treatment chamber accommodating the substrate, a
spin chuck holding the substrate disposed in the treatment
chamber, a coating liquid nozzle for dispensing a coating

liquid to the substrate, a coating liquid dispensing system for dispensing the coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent to the coating liquid nozzle, a 5 solvent nozzle for dispensing the solvent into the treatment chamber, and a solvent dispensing system for dispensing the solvent to the solvent nozzle; an aging unit for gelling the film; and 10 a solvent replacement unit for replacing the solvent in the film.

, 26. A method of forming a film, comprising:
a step of coating, on a surface of a substrate, a solvent which is of lower viscosity than that of the most viscous solvent component of a coating liquid in which 15 particles or colloids of a starting substance of a film component are dispersed in a solvent, and which dissolves the starting substance;
a step of forming a film by coating the coating liquid on the surface of the substrate; and
20 a step of gelling the particles or colloids in the film.

27. The method of forming a film as set forth in claim 26:

wherein a solution of lower viscosity than the most viscous component among the solvent components is one solvent 25 component of the coating liquid.

28. The method of forming a film as set forth in claim 26:

wherein the solution of lower viscosity than that of

the most viscous solvent component is an alcohol.

29. The method of forming a film as set forth in claim 26, further comprising:

a solvent replacement step of dispensing a solvent
5 different from the solvent on the surface of the substrate
thereon the film is formed and gelling treatment is carried
out, and of replacing the solvent in the film by the
different solvent.

30. A coating unit, comprises:

10 a treatment chamber for accommodating a substrate;
a spin chuck for holding the substrate disposed in the
treatment chamber;

a solvent nozzle for dispensing a solvent to the
substrate;

15 a solvent dispensing system for dispensing the solvent
to the solvent nozzle;

a coating liquid nozzle for dispensing a coating liquid
to the substrate dispensed thereon the solvent; and

20 a coating liquid dispensing system for dispensing the
coating liquid in which particles or colloids of a starting
substance of a film component are dispersed in the solvent to
the coating liquid nozzle.

31. An apparatus of forming a film, comprises:

a coating unit comprising a treatment chamber for
25 accommodating a substrate; a spin chuck for holding the
substrate disposed in the treatment chamber; a solvent nozzle
for dispensing a solvent to the substrate; a solvent
dispensing system for dispensing the solvent to the solvent

nozzle; a coating liquid nozzle for dispensing a coating liquid to the substrate dispensed thereon the solvent; and a coating liquid dispensing system for dispensing the coating liquid in which particles or colloid of a starting substance 5 of a film component are dispersed in the solvent to the coating liquid nozzle;

an aging unit for gelling the film; and
a solvent replacement unit for replacing the solvent in the coated film.

10 32. A method of forming a film, comprising:

a step of mixing a first liquid containing particles or colloids of a starting substance of a film component which is insoluble or difficult to be dissolved in water, and water, and a second liquid consisting of an organic solvent in which 15 water and film component dissolve;

a step of, before elapse of film quality deteriorating time after completion of mixing, coating a mixed liquid containing the first liquid and the second liquid on a surface of a substrate; and

20 a step of gelling the particles or colloids in the film coated on the substrate.

33. The method of forming a film as set forth in claim 32:

wherein the film quality deterioration time is 6min.
25 after completion of mixing.

34. A method of forming a film, comprising:
a step of mixing a first liquid containing particles or colloids of a starting substance of a film component which is

insoluble or difficult to be dissolved in water, and water,
and a second liquid consisting of an organic solvent in which
water and the film component dissolve;

a step of, before elapse of film quality deteriorating

5 time which deteriorates quality of the film obtained by
mixing thereof after completion of mixing, coating a mixed
liquid containing the first liquid and the second liquid on a
surface of a substrate;

10 a step of cleaning an inside of a flow path of the
mixing portion and a downstream side thereof by an organic
solvent; and

a step of gelling the particles or colloids in the film
coated on the substrate.

35. The method of forming a film as set forth in claim
15 34:

wherein the film quality deterioration time is 6min.
after completion of mixing.

36. A method of forming a film, comprising:

20 a step of forming a film by coating a coating liquid in
which particles or colloids of a starting substance of a film
component are dispersed in a solvent on a surface of a
substrate;

and

25 a step of gelling the particles or colloids in the film
by exposing the substrate to an ammonia gas;

wherein, in the gelling step, an ammonia gas is
sequentially introduced into at least 2 baths accommodating
ammonia water of an ammonia concentration lower than a

saturated concentration to generate an ammonia gas, the ammonia gas generated in advance is fed to the substrate, thereafter the ammonia gas generated subsequently is fed to the substrate, thereby conductance of the ammonia gas fed to 5 the substrate is kept constant.

37. A method of forming a film, comprising:

a step of forming a film by coating a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent on a surface of a 10 substrate; and

a step of gelling the particles or colloids in the film by exposing the substrate to an ammonia gas;

wherein the gelling step comprises:

a step of carrying in a substance to be treated into a 15 treatment chamber;

a first treatment step of generating the ammonia gas containing water vapor by bubbling the ammonia gas into a first bath reserving ammonia water of an ammonia concentration lower than a saturated concentration and of 20 feeding the ammonia gas into the treatment chamber;

a step of generating the ammonia gas containing water vapor by bubbling an inside of a second bath reserving ammonia water of an ammonia concentration lower than a saturated concentration by the ammonia gas, and of exhausting 25 the ammonia gas without through the treatment chamber;

a second treatment step of switching a gas flow path from the first bath to the treatment chamber to a gas flow path from the second bath to the treatment chamber, and

feeding the ammonia gas generated from the second bath into the treatment chamber; and

a step of replenishing the ammonia water into the treatment chamber.

5 38. The method of forming a film as set forth in claim
37:

wherein the gelling step is a step in which conductance of a flow path when a gas flows through a treatment chamber from a first bath, conductance of a flow path when a gas 10 flows through a first exhaust path from a first bath, conductance of a flow path when a gas flows through a treatment chamber from a second bath, and conductance of a flow path when a gas flows through a second exhaust path from a second bath are made equal.

15 39. A method of forming a film, comprising:

a step of forming a film by coating a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent on a surface of a substrate; and

20 a step of gelling the particles or colloids in the film by exposing the substrate to an ammonia gas;

wherein the gelling step comprises:

a step of, by generating an ammonia gas containing water vapor by bubbling an inside of a first bath where 25 ammonia water of a lower ammonia concentration than a saturated concentration is reserved by the ammonia gas, exhausting the ammonia gas without through a treatment chamber but through a first exhaust path;

a step of carrying in the substance to be treated into the treatment chamber;

5 a first treatment step of, by switching subsequently a flow path of the ammonia gas generated from the first bath from the first exhaust path to the treatment chamber, feeding the ammonia gas into the treatment chamber;

10 a step of, during the first treatment being carried out, by generating the ammonia gas containing water vapor by bubbling the second bath where ammonia water of an ammonia concentration lower than a saturated concentration is reserved by the ammonia gas, exhausting the ammonia gas without through the treatment chamber but through the second exhaust path;

15 a step of, together with switching a gas flow path from the first bath to the treatment chamber to a gas flow path from the second bath to the treatment chamber, by closing the second exhaust path, feeding the ammonia gas generated from the second bath into the treatment chamber; and

20 a step of replenishing the ammonia water into the first bath.

40. The method of forming a film as set forth in claim 39:

wherein, in the gelling step, conductance of a flow path when a gas flows from a first bath through a treatment chamber, conductance of a flow path when a gas flows from a first bath through a first exhaust path, conductance of a flow path when a gas flows from a second bath through a treatment chamber, and conductance of a flow path when a gas

flows from a second bath through a second exhaust path, are made equal.

41. A method of forming a film, comprising:

a step of forming a film by coating, on a surface of a substrate, a coating liquid in which particles or colloids of a starting substance of a film component are dispersed in a solvent; and

a step of gelling the particles or colloids in the film by exposing the substrate to an ammonia gas;

10 wherein the gelling step comprises:

a preparatory exhaust step of exhausting a treatment gas from a gas generating source without through a treatment chamber but through an exhaust path;

15 a step of carrying in an object to be treated into a treatment chamber; and

a step of, by switching a flow path from the exhaust path to the treatment chamber side, treating the object to be treated by feeding the treatment gas from the gas generating source into the treatment chamber;

20 wherein conductance of a flow path from the gas generating source through the treatment chamber and conductance of a flow path through the exhaust path, are made equal.

42. An aging unit, comprises:

25 a treatment chamber accommodating a substrate;

a plurality of ammonia baths reserving ammonia water;

a bubbling gas feeding system for feeding a carrier gas for bubbling to the each ammonia bath;

- a bubbling gas valve for switching the each bubbling
gas feeding system;
- an exhaust system for exhausting a gas generated from
the each ammonia bath;
- 5 an exhaust system valve for switching the each exhaust
system;
- an ammonia gas feeding system for feeding the gas
generated at the each ammonia bath to the treatment chamber;
- an ammonia gas valve for switching the each ammonia gas
10 feeding system; and
- a means of, together with opening sequentially the each
bubbling gas valve, synchronizing with switching of each
bubbling gas valve, closing in turn the each exhaust system
valve, and opening in turn the each ammonia gas valve.
- 15 43. An apparatus of forming a film, comprises:
- a coating unit for coating a coating liquid on a
substrate;
- an aging unit comprising a treatment chamber
accommodating a substrate; a plurality of ammonia baths
20 reserving ammonia water; a bubbling gas feeding system
feeding a carrier gas for bubbling in the each ammonia bath;
 a bubbling gas valve switching the each bubbling gas feeding
system; an exhaust system for exhausting a gas generated from
the each ammonia bath; an exhaust system valve for switching
25 the each exhaust system; an ammonia gas feeding system for
feeding the gas generated at the each ammonia bath to the
treatment chamber; an ammonia gas valve for switching the
each ammonia gas feeding system; and a means of, together

with opening sequentially the each bubbling gas valve,
synchronizing with the switching of the each bubbling gas
valve, closing in turn the each exhaust system, and opening
in turn the each ammonia gas valve; and

5 a solvent replacement unit for replacing solvent in a
film.

44. An apparatus of forming a film, comprises:

a coating portion for forming a film by coating a
coating liquid in which particles or colloids of a starting
10 substance of a film component are dispersed in a solvent on a
substrate;

a gelling treatment portion which is disposed adjacent
to the coating portion and gels the particles or colloids in
the film formed at the coating portion;

15 a plurality of pre-treatment portions for pre-treating
in advance of coating of the coating liquid on a substrate;

a plurality of heating portions for drying the
substrate after treatment at the gelling treatment portion;

20 a receiving portion for receiving the substrate from
the exterior;

a main carrying portion for, together with carrying the
substrate to the coating portion through the pre-treatment
portion after receipt of the substrate from the receiving
portion, carrying the substrate treated at the gelling
25 treatment portion to the later heating portion; and

an auxiliary carrying portion carrying the substrate
coated at the coating portion to the gelling treatment
portion.

45. The apparatus of forming a film as set forth in claim 44, further comprising:

a means for feeding the vapor of the solvent component on a transfer path of the substrate in the auxiliary transfer portion.

46. The apparatus of forming a film as set forth in claim 44, further comprising:

a case for covering the coating portion and the gelling treatment portion, and a means for feeding the vapor of the solvent component into the case.

47. The apparatus of forming a film as set forth in claim 44, further comprising:

a solvent replacement treatment portion which is disposed adjacent to the gelling treatment portion, dispenses a solvent different from the aforementioned solvent to the substrate treated at the gelling portion, and replaces the aforementioned solvent in the film by the different solvent:

wherein the main transfer portion transfers the substrate treated at the solvent replacement portion to the heating portion:

wherein the auxiliary transfer portion transfers the substrate treated at the gelling portion to the solvent replacement portion.